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INVESTIGATION OF DENITRATION REACTIONS OF UNSYMMETRICAL TRINITROTOLUENES TO 2,4-DINITROTOLUENE

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number) Several methods were tested for reductive denitration of 2,4,5-trinitrotoluene to 2,4-dinitrotoluene. Tin-hydrochloric acid and ion-hydrochloric acid gave a 10% yield of the desired material; other reagents gave none.		

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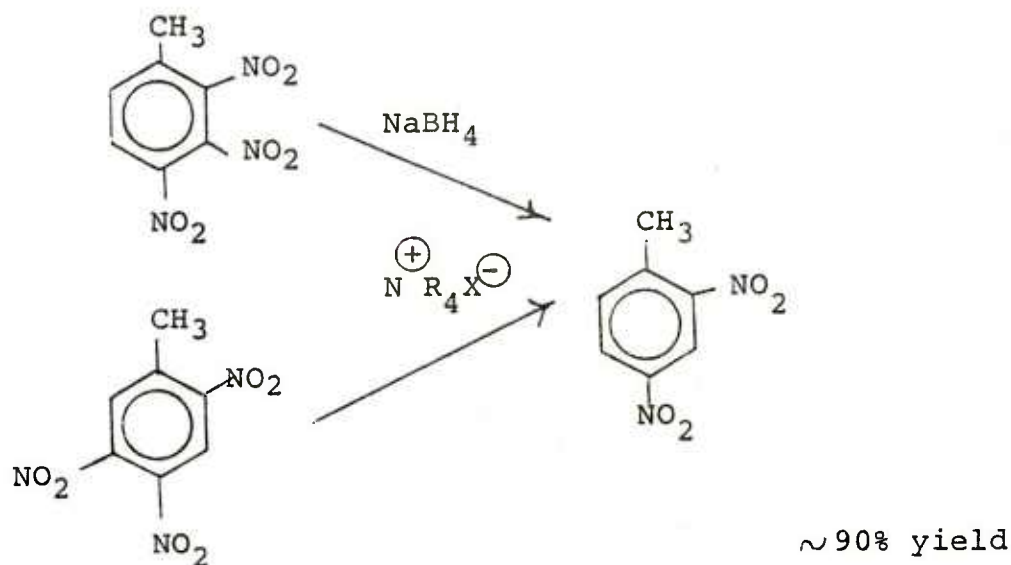
INTRODUCTION

The manufacture of polynitrotoluene compounds for munitions and explosives is a major industry. Large production requirements and the broad variety of manufactured products lead to significant pollution problems. One of the most serious of these is waste which is generated during the manufacture of explosives such as 2,4,6-trinitrotoluene (α -TNT).

During the production of α -TNT, about 4.5% of the crude product comprises objectionable unsymmetrical TNT isomers, principally 2,4,5- and 2,3,4-trinitrotoluenes, which must be removed to achieve suitable munition purity. This is usually done by treating the crude TNT with aqueous sodium sulfite (sellite), which reacts with the isomers forming sodium 2,4-dinitrotoluene-5-sulfonate and 3-sulfonate, respectively. The water soluble sulfonates are removed in the spent sellite solution (red water) in the proportion of about 1.0 part of the 5-isomer to about 0.6 part of the 3-isomer. It has long been recognized that red water presents a disposal problem.

The recrystallization of crude TNT product from concentrated nitric acid can yield a pure α -TNT and unsymmetrical trinitrotoluenes. However, at present these unsymmetrical trinitrotoluenes are not utilized in the U.S.A. Thus, the investigation of the conversion of unsymmetrical trinitrotoluenes to 2,4-dinitrotoluene is of obvious interest because dinitrotoluene can be nitrated further to yield α -TNT or dinitrotoluene can be used as the intermediate for the synthesis of toluene diisocyanate.

Our preliminary experimental results showed¹ that reactions of these unsymmetrical trinitrotoluenes with sodium borohydride in the presence of a cationic surfactant yields 2,4-dinitrotoluene.



Thus, we have initiated a program to investigate further the production of dinitrotoluene from unsymmetrical trinitrotoluenes.

RESULTS AND DISCUSSION

Analytical Procedure

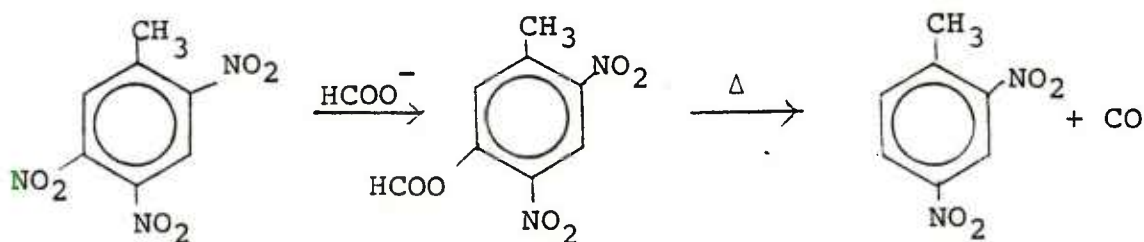
Melting points were taken in a Thomas-Hoover melting point apparatus and are uncorrected; infrared spectra were determined in Nujol mulls with a Perkin-Elmer 457 R spectrophotometer. NMR spectra were obtained with a Varian A-60 spectrometer using tetramethylsilane as internal reference. A Waters Associates ALC-GPC-201 Liquid Chromatograph was used for the quantitative determination of trinitrotoluene isomers and dinitrotoluene. A CN- μ bondapak column was employed with a mixture of

cyclohexane and methylene chloride (9:1) as a mobile phase at the flow rate 1.9 ml per minute with the resulting pressure of 1000 psi, UV detector (254 nm wavelength monitor) set at 0.1 Absorbance Units Full Scale sensitivity.

Materials

Trinitrotoluenes. 2,4,6-Trinitrotoluene was obtained from Eastman Organic Chemicals and recrystallized from ethanol solution, m.p. 82°C. 2,3,4- and 2,4,5-trinitrotoluenes were synthesized by the methods described in the literature, m.p. 112°C (111°C)², m.p. 105°C (104.5°C)², respectively. Other chemical reagents were obtained from commercial sources.

Study of the formation of 2,4-dinitrotoluene via formate derivatives. It is reported in the literature that formic acid and some of its derivatives are excellent donors of hydride in hydride transfer reactions³. The possibility exists that the hydride transfer takes place intramolecularly within the formate ester. Thus, we attempted to study the denitration reactions of 2,4,5-trinitrotoluene to 2,4-dinitrotoluene via the formate derivative as shown in the following equation:



A number of experiments for the synthesis of 2,4-dinitro-5-methyl phenyl formate from 2,4,5-trinitrotoluene were carried out. Typical examples of the reactions investigated follow:

a) Reaction of 2,4,5-trinitrotoluene with HCOONa in p-dioxane

The trinitrotoluene 4.57g was dissolved in dioxane (250 ml) and then HCOONa (5.44 g) was added. The reaction mixture was stirred with a magnetic stirrer and refluxed for 18 hours. After the insoluble compound was filtered, the filtrate was evaporated under reduced pressure. The gummy product obtained was recrystallized from ethanol and found to be identical with the trinitrotoluene (recovered 85%). During the reaction, a small white solid (0.025g) was sublimed and condensed on the wall of the condenser. The compound melted at 154°C. This compound was not identified.

b) Reaction of 2,4,5-trinitrotoluene with HCOOK in the presence of the crown ether (dibenzo 18-crown-6) in benzene solution

Macrocyclic polyethers of the type exemplified by 18-crown-6 have the extraordinary ability to form stable molecular complexes with cations, owing to the efficient coordination of the cation by the ether oxygens⁴. 18-Crown-6 has a cavity diameter estimated to be between 2.6.Å and 3.2.Å. It therefore complexes most strongly with K^+ which has an ionic diameter of 2.66.Å. The dissociated formate anion from the cation upon formation of the complex becomes highly reactive. Thus the reaction of the trinitrotoluene with HCOOK in the presence of dibenzo 18-crown-6 in benzene was investigated. The trinitrotoluene (2.28g, 0.01 mole), HCOOK (0.04 mole) and the crown ether (0.0005 mole) were dissolved in 100 ml benzene. The solution was refluxed overnight and the color of the

reaction mixture became dark brown. The dark colored solid was precipitated and found to be sparingly soluble in organic solvents such as CCl_4 , CHCl_3 , H_2O , CH_3CN and acetone. The solid melted at 200°C . The IR spectra of the compound indicated that it is a polymeric aromatic nitro compound. The exact structure has not yet been determined.

c) Reaction of 2,4,5-trinitrotoluene with HCOOK in HCOOH

The trinitrotoluene (4.57g, 0.02 mole) and HCOOK (6.72g, 0.16 mole) were dissolved in formic acid (125 ml) and the solution was refluxed for 24 hours. After the formic acid was evaporated under reduced pressure, the residue was washed with a large amount of water and then recrystallized from ab. ethanol. The yellow solid obtained melted at $74-76^\circ\text{C}$. The compound (3.4g) was obtained and the yield 2,4-dinitro 5-methyl phenyl formate was about 80%. The IR and nmr spectra of the compound corresponded to the formate ester.

d) Reaction of 2,4,5-trinitrotoluene with HCOOK in CH_3CN

The mixture of the trinitrotoluene (0.01 mole) and HCOOK (0.08 mole) in CH_3CN (50 ml) was refluxed for 24 hours. After treating the reaction product as described in (c), the product was recrystallized from ethanol and melted at 75°C . The IR and nmr spectra were identified as the corresponding formate. However, the yield of the reaction was found to be 40%.

e) Reaction of 2,4,5-trinitrotoluene with HCOOK in water

The heterogeneous mixture of the trinitrotoluene (4.5g, 0.02 mole) and HCOOK (0.16 mole) in water (15 ml) was heated at the refluxing temperature for 18 hours. After removing the

water, the product was washed with a large amount of water. The solid, 1.3 g, was isolated and found to be sparingly soluble in CHCl_3 , water CH_3CN and acetone. It melted at 200°C . The IR and nmr spectra of the compound indicated that the product was identical with the compound in reaction (b).

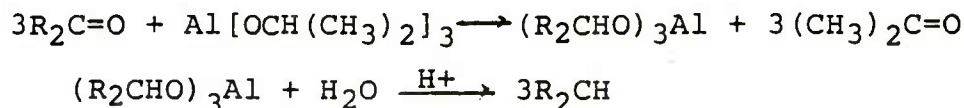
f) The decomposition of 2,4-dinitro 5-methyl phenyl formate

The thermal decompositions of the formate were carried out under several conditions. It was found that the compound was thermally stable and did not decompose to the dinitro-toluene (e.g., 140°C for 3 hours).

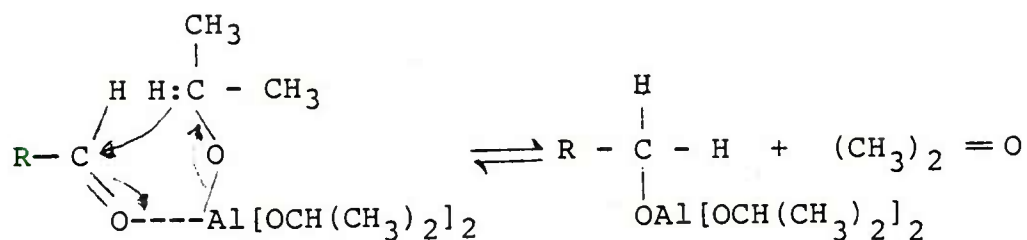
Reaction of 2,4,5 trinitrotoluene with aluminum isopropoxide

In 1926 Meerwein-Ponndorf reported a method of hydride transfer reaction using aluminum isopropoxide⁵. Aluminum alkoxides are much less polar than alkali metal alkoxides, the aluminum-oxygen bonds being almost covalent and having little tendency to dissociate to give free alkoxide ions. Aluminum isopropoxide, the reagent of choice, is a low melting solid (118°C) which distills at 140 to 150°C under 12 mm Hg.

Aluminum isopropoxide was used to reduce aldehydes and ketones to corresponding alcohols.



The mechanism of reduction probably involves, first, association of the carbonyl oxygen with aluminum and then transfer of the hydride ion in a cyclic transition state. Thus, for the reduction of RCHO :



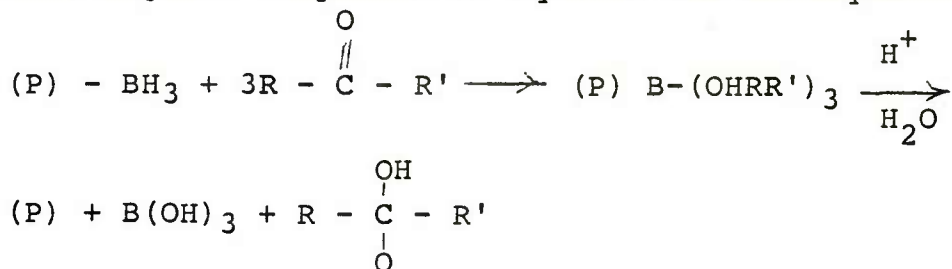
Similar hydride transfer was considered to have taken place in the hydride displacement of the labile nitro group in the trinitrotoluene with aluminum isopropoxide.

Thus, several experiments were carried out on the reactions of 2,4,5-trinitrotoluene with aluminum isopropoxide. Typical examples of the results are summarized as follows:

2,4,5-Trinitrotoluene, 4.5 g (0.02 mole) was dissolved in 40 ml of acetone free isopropyl alcohol in a 100 ml three-necked round bottomed flask. The flask was attached to a short refluxing column and water condenser to distill off any acetone formed during the reaction. Freshly prepared aluminum isopropoxide, 4.0 g, was added to the flask and the reaction was refluxed. The color of the solution immediately turned blue and then became dark red. After the solution was refluxed for 1.5 hrs and the mixture cooled to room temperature, the solution was acidified with 10 ml of dilute HCl. A fine solid was precipitated, which was filtered, washed with water and dried. The solid was 4.0 g and melted at 105°C. The solid obtained was found to exhibit no melting point depression with pure 2,4,5-trinitrotoluene and the IR spectrum was identified as that of 2,4,5-trinitrotoluene. Thus, in conclusion, the reaction had not taken place and the unreacted compound was recovered in 90% yield.

Reaction of unsymmetrical trinitrotoluene with
polymeric amine-borane (Amborane)

Recently Rohm and Haas Company has manufactured Amborane resin⁶. Amborane is a highly porous, solid phase, polymeric amine-borane reducing agent. The boron hydride moiety attached to a polymeric matrix has been used in reduction of various organic compounds in aqueous and non-aqueous solvents,



where (P) is the polymer matrix.

Thus we investigated the possibility that the resin might be used in replacement of the nitro group at the meta position of unsymmetrical trinitrotoluenes by hydride, to yield 2,4-dinitrotoluene.

Amborane 345 is a mild reducing agent which is comparable to monomeric amine-boranes, but offers greater stability, selectivity and processing advantages for precious metal recovery and organic reduction. It is acrylic-based and is supplied as a spherical particle usable in a column or batch type operation. We obtained 50 g of Amborane 345 from Ventron Division, Alfa Products.

Amborane 345, 25 g, was mixed with 75 ml of tetrahydrofuran and poured into a 9" x 1^{1/2}" glass column. 2,4,5-Tri-
nitrotoluene, 1 g, ^{was} dissolved in 75 ml of tetrahydrofuran and allowed to pass through the column at a rate of 5 ml/1 min

at room temperature. Initially there was no change in the color of the column nor of the eluting solution, but after 10-15 min. the color started changing to red. The eluted samples were analyzed by liquid chromatograph. Typical data is shown in Table 1.

Table 1. Analysis of Product by Liquid Chromatograph

	<u>2,4-Dinitrotoluene %</u>
1st cycle	0.0
2nd cycle	5.0
3rd cycle	12.0
4th cycle	15.0
5th cycle	18.0

The 5th cycle solution was acidified with dilute HCl and then tetrahydrofuran was evaporated on a rotatory evaporator. The residue was extracted with methylene chloride and the solution was dried over MgSO_4 . After evaporation CH_2Cl_2 and recrystallization of product, a solid, 0.1 g, was isolated and identified as 2,4-dinitrotoluene by IR and mixed melting point measurements.

The other experiment on the reaction of 2,4,5-trinitrotoluene with Amborane 345 using a batch process in THF-methanol

solvent gave 2,4-dinitrotoluene in good yield (~90%).

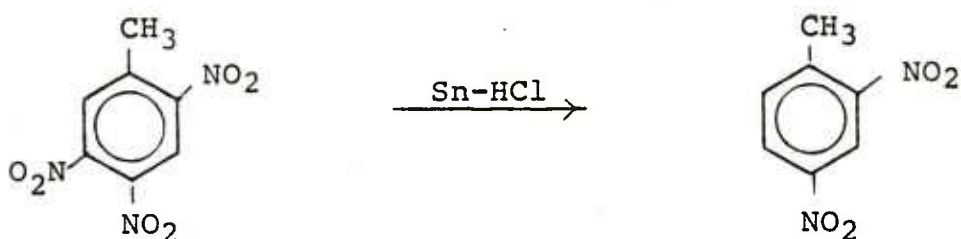
These results show that the nitro group at the meta position of unsymmetrical trinitrotoluene can be replaced with hydride using Amborane resin. The reaction process was found to be very simple and relatively pure product, 2,4-dinitrotoluene could be obtained from the trinitrotoluene. However, at present, the price of Amborane resin is high and the process may not have a great advantage over the previous hydride-replacement " BaBH_4 -phase transfer" process.

Reaction of 2,4,5-trinitrotoluene with Sn-HCl

The most important synthetic reaction of nitro groups involves reduction, particularly to the amine level. In fact, aromatic amines are normally prepared by nitration, followed by reduction. Despite the complexity of the reaction, reduction of aromatic nitro compounds to amines occurs smoothly in acid

solution with a variety of reducing agents of which tin metal and hydrochloric acid or stannous chloride are often favored on a laboratory scale.

It was considered that the reduction system may replace the labile nitro group at the meta position of 2,4,5-trinitrotoluene under mild conditions. Thus, several experiments were carried



out on the reaction of 2,4,5-trinitrotoluene with Sn-HCl. Typical examples of the results are summarized as follows.

2,4,5-Trinitrotoluene, 4.5 g, (0.02 mole) was dissolved in 300 ml of 95% ethanol. The solution was cooled to 0°C in an ice-bath. Granulated Sn powder, 5.0 g, (0.22 mole) was added to the solution and then stirred. Hydrogen chloride (6N) 11 ml was added dropwise over 15-20 min. The reaction was exothermic and the color of the solution turned dark red. After 1.5 hrs reaction period, the reaction mixture was filtered and some ethanol was evaporated (concentrated to 20 ml) under reduced pressure. The residue was poured into 500 ml of water and the product extracted with methylene chloride. After the methylene chloride solution was dried over MgSO₄, the product was analyzed by high

pressure liquid chromatography (HPLC). Four major products were detected, one of which corresponded to 2,4-dinitrotoluene. Thin layer chromatography (TLC) also showed four different spots and one corresponded to 2,4-dinitrotoluene. The methylene chloride was evaporated and an oily residue, 2.92 g, was obtained. An attempt was made to separate the mixture by column chromatography on silica gel. The first elution with pentane gave 0.8 g of a solid which melted at 84°C. The HPLC and TLC were identified as corresponding to 2,4-dinitrotoluene. The other three compounds were also isolated in small yield, m.p. 150°, 215° and 250°C. The structures of these compounds were not determined.

The reactions of 2,4,5-trinitrotoluene with Sn-HCl were also carried out in a solvent mixture of isopropyl alcohol and tetrahydrofuran at 0°C. After similar treatment as described above, the residue was dried and the solvent removed under reduced pressure. During the operation, the compound EXPLODED!

The extraction was also performed with diethyl ether instead of methylene chloride - the residue EXPLODED!

The dried residue exploded in both experiments, perhaps due to formation of diazo compounds.

Reaction of 2,4,5-trinitrotoluene with Fe-HCl

Trinitrotoluene, 4.5 g, (0.02 mole) was dissolved in a 150 ml solution of ethanol and dichloromethane (1:1 vol). The solution was cooled to 0°C in an ice-bath. Granulated Fe powder, 5 g, was added to the solution and then stirred. HCl (6N) 12 ml was added dropwise over 20~30 min. The reaction was exothermic and the color of the solution turned dark red.

After a 2 hour reaction period, the reaction mixture was filtered. The resulting product was analyzed by a procedure similar to that described above for Sn-HCl experiments. The HPLC analysis showed that a product corresponding to 2,4-dinitrotoluene contained about 10% (weight) with two other products (unidentified) having a 3-4 times greater amount than that of the dinitrotoluene detected. Attempts to improve the yield of dinitrotoluene using various conditions of the Fe-HCl system were unsuccessful.

Reactions of 2,4,5-trinitrotoluene with Zn-HCl

Similar reactions as in the Sn-HCl and Fe-HCl systems were carried out using Zn instead of Sn and Fe. In all the experiments performed, no dinitrotoluene was produced.

Reactions of 2,4,5-trinitrotoluene with Zinc amalgam-HCl

Reactions were carried out using zinc amalgam with HCl in organic solvents such as toluene and ethanol-methylene chloride mixtures. No detectable dinitrotoluene was obtained.

Reactions of 2,4,5-trinitrotoluene with CaH₂

Trinitrotoluene, 1g, was dissolved in 3 ml THF. To the solution 3g CaH₂ was added and stirred for several hours at room temperature. The solution turned dark orange. Analysis of the solution showed that there was no dinitrotoluene produced. An additional 1g of fresh CaH₂ was added to the mixture and it was refluxed using a steam bath for 5 hours. The solution turned dark red. No detectable dinitrotoluene was obtained.

Reactions of 2,4,5-trinitrotoluene with Zn in acetic acid

The trinitrotoluene, 1.0 g, was dissolved in 50 ml of glacial acetic acid. The solution was cooled to 0°C and 1.0 g Zn powder was added slowly. After 4 hours of stirring at 0°C, the mixture was filtered and water (100 ml) added. The product was extracted with dichloromethane and analyzed by HPLC. No detectable dinitrotoluene was produced by this system.

Reactions of 2,4,5-trinitrotoluene with triethyl phosphite

Trinitrotoluene, 1.0 g, was dissolved in 40 ml methanol and cooled to 0°C. Triethylphosphite, 1 g, was added dropwise with stirring. After 1 hour, there was no dinitrotoluene produced. After adding a further 1 g of triethylphosphite, the reaction was allowed to run for 2 hours at 0°C. No detectable dinitrotoluene was obtained and unreacted trinitrotoluene was recovered.

Reactions of 2,4,5-trinitrotoluene with Zn-Ammonium chloride

Trinitrotoluene (1.0 g) was dissolved in a 75% aqueous ethanol solution containing 1.0 g ammonium chloride. Zn powder (2.0 g) was slowly added to the solution at room temperature (25°C). The mixture turned dark red. After 45 minutes, the analysis revealed that considerable trinitrotoluene was reacted, but no detectable dinitrotoluene was produced.

Conclusions and Recommendations

1. Several different methods for denitration reactions of unsymmetrical trinitrotoluenes to 2,4-dinitrotoluene have been studied.
2. Reaction of 2,4,5-trinitrotoluene with Sn-HCl gave about 10% 2,4-dinitrotoluene (analyzed by liquid chromatography). The solid products isolated occasionally exploded. The exact reason for the explosions was not determined. The product was red and contained a diazo compound.
3. Reaction of 2,4,5-trinitrotoluene with Fe-HCl also yielded about 10% 2,4-dinitrotoluene. However, other products were 3-4 times greater than that of 2,4-dinitrotoluene.
4. Reactions of 2,4,5-trinitrotoluene with Zn-HCl, Zn-amalgam-HCl, Zn-acetic acid, Zn-ammonium chloride and triethylphosphite did not produce a detectable amount of dinitrotoluene.
5. Reaction of 2,4,5-trinitrotoluene with aluminum isopropoxide did not produce a detectable amount of dinitrotoluene.
6. Investigation of the formation of 2,4-dinitrotoluene via formate derivatives was not successful.
7. Reaction of 2,4,5-trinitrotoluene with Amborane (polymeric amine-borane) yielded 2,4-dinitrotoluene (90% yield).

8. The results obtained to date show that the best method for the denitration of unsymmetrical trinitrotoluene to 2,4-dinitrotoluene is still the hydride replacement " NaBH_4 -phase transfer" process. However, at present this process is not economical.
9. Further work on methods of direct denitration of unsymmetrical trinitrotoluene appears warranted and should be carried out by electrochemical reduction and photochemical denitration reactions.

References

- (1) Y. Okamoto and S.T. Attarwala, J. Org. Chem., 44, 3269(1979).
- (2) W. H. Dennis, D. H. Rosenblatt, W. G. Blucher and C. L. Coon, J. Chem. Eng. Data, 20, 2 (1975).
- (3) N. C. Deno, H. J. Peterson and G. S. Saines, Chem. Revs. 60, 7 (1960).
- (4) C. J. Pederson and H. K. Frendorff, Angew Chem., Interal. 11, 16 (1972).
- (5) A. L. Wilds, Organic Reactions, 2, 178 (1944).
- (6) AmboraneTM 345 Reductive Resin, Rohm & Haas Company, June 1980.

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